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DEVELOPMENT OF A GLASS MATRIX COMPOSITION FOR SINGLE-LAYER WHITE LOW-MELTING ENAMEL FOR STEEL

A. P. Zubekhin,¹ V. A. Guzii,¹ A. V. Ryabova,¹ E. A. Yatsenko,¹ and E. V. Filatova¹

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Based on the $R_2O - B_2O_3 - Al_2O_3 - SiO_2 - TiO_2 - P_2O_5$ system, the regions of formation of low-melting glass matrices are determined. The relationship between the opacifying capacity of the synthesized glasses and the quantities of SiO_2 , B_2O_3 , and R_2O and their ratios is determined. A glass matrix composition is identified which is used as a white enamel to protect and to impart a decorative outlook to steel facing sheets.

The technology of low-temperature single-layer enameling can be effective in protecting household gas and electric equipment containing large steel sheet parts against deformation [1].

This important scientific and practical problem can be solved by synthesis of white low-melting glass enamel which, primarily, ensures sufficient adhesion to steel in low-temperature firing (not greater than 720°C) in the absence of priming enamel and, second, has good whiteness (at least 83% by MS-20) and sufficient chemical resistance.

An analysis of the known compositions of white low-melting single-layer enamels for steel [1, 2] shows that the available enamels have a relatively high melting point and are synthesized in a fluorine-containing system: $R_2O - RO - B_2O_3 - SiO_2 - TiO_2 - P_2O_5 - F^-$. In the context of current environmental requirements, it is necessary to exclude the use of fluorine and at the same time to provide for a low melting point of the enamel.

A fluorine-free system $R_2O - B_2O - Al_2O_3 - SiO_2 - TiO_2 - P_2O_5$ was chosen as the basis for the development of a glass matrix (frit) for single-layer white enamel. The initial conditions of the glass matrix synthesis were as follows: the content of glass-forming oxides (SiO_2 and B_2O_3) and modifiers was within the following limits (%), here and elsewhere weight content is indicated: 25–40 SiO_2 , 5–25 B_2O_3 , 25–40 R_2O . With the aim of ensuring the maximum polyalkaline effect in the absence of alkaline-earth oxides, to provide for the maximum fusibility, and to optimize the matrix structure, the ratio of $Na_2O : K_2O : Li_2O$ was taken equal to 1.0 : 0.6 : 0.4. To ensure high whiteness of the enamel, it is necessary to accomplish optimum opacification of the glass; therefore, TiO_2 was introduced into the glass composition with this object in view. In order to determine the relation-

ship between the composition of the glass and its opacifying capacity, the amount of opacifier TiO_2 and oxides facilitating opacification (Al_2O_3 and P_2O_5) was kept constant (%): 16 TiO_2 , 2 Al_2O_3 , 2 P_2O_5 .

The compositions of 18 glasses that were synthesized are given in Table 1.

As is usual for low-temperature enameling technology, the glasses were melted at temperatures 1150–1200°C with 0.5 h holding and air cooling of the melt.

Visual and microscope analysis of the quality of the produced samples indicated that all glasses were well melted and located in a certain region of the pseudotriple system:

TABLE 1

| Glass composition | Weight content, %* | | | | |
|-------------------|--------------------|--------|---------|---------|----------|
| | Na_2O | K_2O | Li_2O | SiO_2 | B_2O_3 |
| 1 | 18 | 10 | 7 | 40 | 5 |
| 2 | 15 | 9 | 6 | 40 | 10 |
| 3 | 13 | 7 | 5 | 40 | 15 |
| 4 | 20 | 12 | 8 | 35 | 5 |
| 5 | 18 | 10 | 7 | 35 | 10 |
| 6 | 15 | 9 | 6 | 35 | 15 |
| 7 | 13 | 7 | 5 | 35 | 20 |
| 8 | 18 | 11 | 7 | 32 | 12 |
| 9 | 17 | 10 | 7 | 30 | 16 |
| 10 | 20 | 12 | 8 | 30 | 10 |
| 11 | 16 | 10 | 6 | 30 | 18 |
| 12 | 18 | 11 | 7 | 30 | 14 |
| 13 | 19 | 11 | 8 | 30 | 16 |
| 14 | 15 | 9 | 6 | 30 | 20 |
| 15 | 19 | 12 | 7 | 27 | 15 |
| 16 | 21 | 12 | 8 | 28 | 12 |
| 17 | 20 | 12 | 8 | 25 | 15 |
| 18 | 18 | 10 | 7 | 25 | 20 |

* All composition contained 16% TiO_2 , 2% Al_2O_3 , and 2% P_2O_5 .

¹ South-Russian Technical University (NPI), Novocherkassk, Russia.

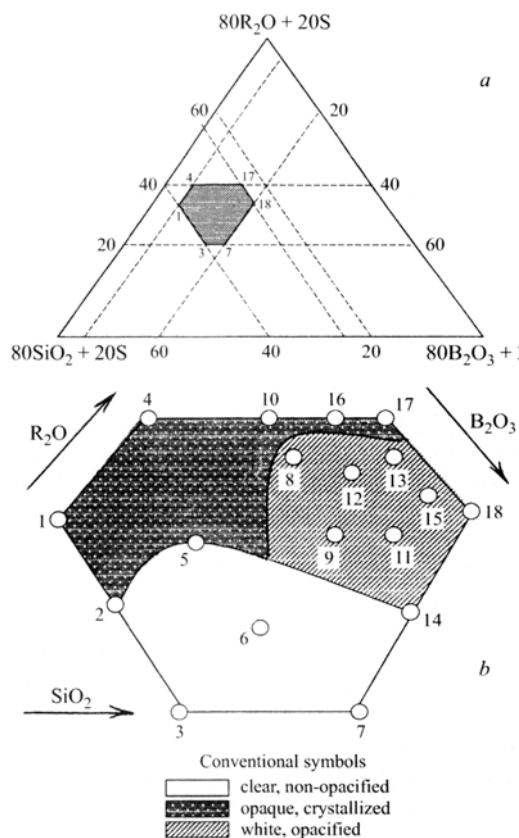


Fig. 1. Region of low-melting glass in the $R_2O - B_2O_3 - Al_2O_3 - SiO_2 - TiO_2 - P_2O_5$ system (a) and clarity of glasses of different compositions in this system (b): 1 – 18) glass compositions (see Table 1).

$80SiO_2 + 20S - 80B_2O_3 + 20S - 80R_2O + 20S$ ($S = 16TiO_2 + 2Al_2O_3 + 2P_2O_5$, $R_2O = Na_2O : K_2O : Li_2O = 1.0 : 0.6 : 0.4$). The glasses differ only in their color shades (from yellow to clear) and the degree of opacification (Fig. 1).

With the purpose of producing white enamel, the type and whiteness of glass matrices in relation to their composition were studied through heat treatment of glasses at $700^\circ C$ for 10 min. As can be seen in Fig. 1, glass matrices 2, 3, 6, 7,

and 14 are totally devoid of opacification; glass matrices 1, 4, 5, 10, 16, and 17 are opaque and crystallized; glass compositions 8, 9, 11, 12, 13, 15, and 18 exhibit uniform opacification and good whiteness (83 – 85% by MS-20 scale) and luster (58 – 60%).

Since all the glasses contain equal quantities of opacifying oxides (TiO_2 and P_2O_5), it is obvious that the opacifying capacity of glass matrices is affected not only by these oxides, but also by SiO_2 , B_2O_3 , R_2O , and their ratio ($SiO_2 + B_2O_3)/R_2O$, which determines the glass structure and the crystalline-chemical state of titanium ions in this structure. The formation of a certain crystalline titanium-containing phase in the heat treatment of glass is possible when titanium ions act as structural modifiers, and the structure is characterized by a decreased level of association of the $[SiO_4]$ and $[BO_4]$ tetrahedra in the special lattice. This is accomplished with the $(SiO_2 + B_2O_3)/R_2O$ ratio equal to 0.9 – 1.3 in glass compositions 8, 9, 11, 12, 13, 15, and 18, which have the optimum opacification and provide for production of white low-melting enamel with good luster.

The most suitable glass for single-layer enameling of large steel sheet parts, which produces white glass enamel coating with good gloss, is glass matrix 13 (a patent for this composition has been filed in the Russian Federation, and a positive decision has been made). The enamel based on the developed glass matrix was tested in experimental industrial production and its high quality was confirmed.

The developed glass enamel coating can be used to protect and to impart an attractive outlook to steel facing parts of household equipment and other products which do not experience high mechanical loads in service.

REFERENCES

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2. A. V. Ryabova, "White low-melting single-layer glass-enamel coatings for steel," *Author's Abstract of Candidate's Thesis [in Russian]*, Belgorod (1999).